

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the INPIT, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

1. Untranslatable words are replaced with asterisks (* **).
2. Texts in the figures are not translated and shown as it is.

Translated: 22:27:12 JST 03/02/2009

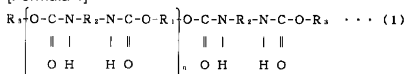
Dictionary: Last updated 02/13/2009 / Priority: 1. Chemistry / 2. Natural sciences / 3. Industrial Products

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] [the end isocyanate group content compound of the reactant of a hydrogenation polybutadiene polyol (a1) and a polyisocyanate (a2)] The urethane (meta) acrylate system resin [A] which is obtained by making hydroxyl group content (meta) acrylate (a3) react and which is shown with a following general formula (1), The activity energy line hardening type pressure sensitive adhesive composition which contains with a carbon numbers of six or more aliphatic series or alicycle group alkyl acrylate [B], and is characterized by things.

[Formula 1]



Here, as for R₁, the both-ends urethane bond residue of a polyisocyanate (a2) and R₃ are the urethane bond residues of hydroxyl group content (meta) acrylate (a3) the both-ends urethane bond residue of a hydrogenation polybutadiene polyol (a1), and R₂, and n is one or more integers.

[Claim 2] The activity energy line hardening type pressure sensitive adhesive composition according to claim 1 characterized by n using urethane acrylate system resin of 2-5 as urethane (meta) acrylate system resin [A].

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an activity energy line hardening type pressure sensitive adhesive composition useful on protection films, such as a pressure sensitive

adhesive composition which hardens with activity energy lines, such as ultraviolet radiation, and discovers an adhesion function, especially an automotive body.

[0002]

[Description of the Prior Art] While it is requested that exfoliation should not be caused to an automotive body paint film, or a crack should not be given to it as a binder used for protection films, such as an automotive body which the demand is increasing recently, since there is much storage on the outdoors etc., weatherability is also required. Although acrylic resin and rubber system resin are conventionally used abundantly as this binder, there are merits and demerits in respect of balance with adhesion with a base material, or weatherability, and the improvement is required. Moreover, since conventional acrylic resin and rubber system resin are a solvent type thing, they usually have the room of correspondence also from a point of an environmental problem.

[0003] On the other hand, examination of activity energy line hardening type adhesives or a binder is made from a predominance that hardening is completed very much by the exposure of short-time ultraviolet radiation etc. For example, in JP,H6-184498,A, the hardened type adhesives constituent which consists of at least one sort chosen from the group which consists of acrylic acid (meta) and carboxyl content (meta) acrylate, and polyurethane poly(meta) acrylate is indicated. It is indicated that the bond strength to a film is demonstrated and this adhesives constituent is used as adhesives for a lamination by carrying out electron radiation curing. Moreover, in JP,H11-189762,A, it is indicated that the resin composition thing which consists of urethane acrylate which consists of polyester polyol, a polyisocyanate, and mono-hydroxyalkyl acrylate, and reactive diluent is used as a resin composition thing for pressure sensitive adhesive sheet base materials. Furthermore, in JP,H4-183770,A, the urethane (meta) acrylate oligomer and monofunctional (meta) acrylate which are obtained by making acrylate react to the hydroxyl group in the reactant of a hydrogenation polybutadiene polyol and a polyisocyanate are contained. The becoming radiation-curing type pressure sensitive adhesive composition is indicated.

[0004]

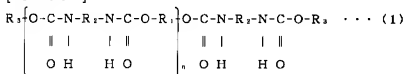
[Problem(s) to be Solved by the Invention] Then, although this invention person etc. inquired that the activity energy line hardening type resin composition thing known until now also including the above-mentioned gazette indication technology should be applied to the above-mentioned binder for protection films There is nothing that was able to take the moderate balance of an adhesive property with a base material and weatherability, and the development is just going to desire. In this invention, it excels in the balance of an adhesive property with a base material, and weatherability under such a background, and aims at offering an activity energy line hardening type pressure sensitive adhesive composition useful as a binder used for various protection films.

[0005]

[Means for Solving the Problem] However, as a result of repeating research wholeheartedly in view of this situation, this invention person etc. [the end isocyanate group content compound of the reactant of a hydrogenation polybutadiene polyol (a1) and a polyisocyanate (a2)] The urethane (meta) acrylate system resin [A] which is obtained by making hydroxyl group content (meta) acrylate (a3) react and which is shown with a following general formula (1), As the activity energy line hardening type pressure sensitive adhesive composition containing with a carbon numbers of six or more aliphatic series or alicycle group alkyl acrylate [B], especially urethane (meta) acrylate system resin [A] When n used urethane (meta) acrylate system resin of 2-5, it found out agreeing for the above-mentioned purpose, and this invention was completed.

[0006]

[Formula 2]



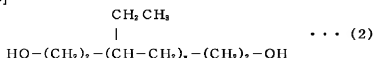
Here, as for R1, the both-ends urethane bond residue of a polyisocyanate (a2) and R3 are the urethane bond residues of hydroxyl group content (meta) acrylate (a3) the both-ends urethane bond residue of a hydrogenation polybutadiene polyol (a1), and R2, and n is one or more integers.

[0007]

[Embodiment of the Invention] This invention is explained in detail hereafter. The urethane (meta) acrylate system resin [A] used by this invention is the thing of the constitutional formula shown with the above-mentioned general formula (1). What is necessary is to just be obtained by making hydroxyl group content (meta) acrylate (a3) react to the end isocyanate group content compound of the reactant of a hydrogenation polybutadiene polyol (a1) and a polyisocyanate (a2).

[0008] the hydrogenation polybutadiene polyol (a1) used by this invention is what is shown with a following general formula (2) -- the molecular weight -- 300-6000 -- the thing of 500-3000 is preferably useful. moreover, an iodine number -- 0-50 -- it is 0-20 preferably and 30 - 250 KOHmg/g is preferably suitable for a hydroxyl value 15 to 400 KOHmg/g.

[0009]



Here, m is the integer of 3-110.

[0010] In this invention, you may use other polyols together if needed in addition to a hydrogenation polybutadiene polyol (a1). For example, ethylene glycol, diethylene glycol, triethylene glycol, Tetraethylene glycol, polyethylene glycol, propylene glycol, Dipropylene glycol, polypropylene glycol, butylene glycol, 1, 4-butanediol, a polybutylene glycol, 1,6-dihydroxyhexane, Neopentyl glycol, cyclohexane dimethanol, hydrogenation bisphenol A, Poly caprolactone, trimethylolethane, trimethylol propane, Poly trimethylol propane, pentaerythritol, the poly pentaerythritol, Sorbitol, mannitol, arabitol, xylitol, galactitol, Polyhydric alcohols, such as glycerol, polyglycerin, and a polytetramethylene glycol, The polyether polyol which has the block of polyethylene oxide, polypropylene oxide, and ethyleneoxide/propylene oxide, or at least one sort of structures of random copolymerization, this polyhydric alcohol, or polyether polyol and maleic anhydride Maleic acid, boletic acid, itaconic acid anhydride, itaconic acid, adipic acid, Caprolactone denaturation polyols, such as polyester polyol and a caprolactone denaturation polytetramethylene polyol, a polyolefine system polyol, etc. which are a condensate with polybasic acid, such as isophthalic acid, are mentioned.

[0011] Especially as a polyisocyanate (a2), for example, without being limited An aromatic series, Polyisocyanates, such as an aliphatic series system and an alicyclic system, are mentioned, and especially Tolyene diisocyanate, Diphenylmethane diisocyanate, hydrogenation-ized diphenylmethane diisocyanate, Denaturation diphenylmethane diisocyanate, hydrogenation-ized xylylene diisocyanate, Xylylene diisocyanate, hexamethylene di-isocyanate, trimethyl hexamethylene di-isocyanate, Diisocyanate or these trimers, such as tetramethyl xylylene diisocyanate, isophorone diisocyanate, norbornene diisocyanate, 1, and 3-bis(isocyanato methyl) cyclohexane, etc. are used suitably. As for the molecular weight of this polyisocyanate compound (a2), 150-700 are desirable from a reactant point with a hydroxyl group.

[0012] As hydroxyl group content (meta) acrylate (a3) For example, without being limited especially 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, 2-hydroxyethyl acryloyl phosphate, 4-butyl hydroxy (meta) acrylate, 2-(meta) AKURIRO yloxy ethyl 2-hydroxypropyl phthalate, GURISERINJI (meta) acrylate, 2-hydroxy 3-AKURIRO yloxy propyl (meta) acrylate, Caprolactone denaturation 2-hydroxyethyl (meta) acrylate, pentaerythritol bird (meta) acrylate, dipentaerythritol penta (meta) acrylate, caprolactone denaturation 2-hydroxyethyl (meta) acrylate, etc. are mentioned. The alkyl (meta) acrylate of 2-20 has the useful carbon number of an alkyl group in respect of tackiness and weatherability also in these.

[0013] [process / of the urethane (meta) acrylate system resin [A] used by this invention] A hydrogenation polybutadiene polyol (a1) and a polyisocyanate (a2) are made to react from the stability of reaction control, and a viewpoint of shortening of production time. After obtaining an end isocyanate group content compound, subsequently to this end isocyanate group content

compound, the method to which hydroxyl group content (meta) acrylate (a3) is made to react is used.

[0014] After making a hydrogenation polybutadiene polyol (a1) and a polyisocyanate (a2) react in the above-mentioned method by the reaction molar ratio of k:k +1 (molar ratio) (k is one or more integers.), Furthermore, it is desirable to make hydroxyl group content (meta) acrylate (a3) react to this end isocyanate group content compound by the reaction molar ratio of 1:2. In these reactions, it is also desirable to use catalysts, such as dibutyltin dilaurate, in order to promote a reaction.

[0015] although urethane (meta) acrylate system resin [A] is obtained in this way, it is desirable that the weight average molecular weights of urethane (meta) acrylate system resin [A] are 5,000-100,000 in this invention -- further -- it is desirable that it is 10,000-30,000. Coating nature worsens and is not desirable, if tackiness becomes low by less than 5,000 and this weight average molecular weight exceeds 100,000.

[0016] In addition, the above-mentioned weight average molecular weight is a weight average molecular weight by standard polystyrene molecular weight conversion. [high performance chromatography (the Showa Denko K.K. make, "ShodexGPC system-11 type") Column: Shodex GPC It is measured by using 3 series of KF-806L (exclusion-limit molecular weight: 2x10⁷, separation range:100-2x10⁷, theoretical plate number:10,000 step/a book, bulking agent quality-of-the-material:styrene divinylbenzene copolymer, bulking agent grain size:10micrometer).

[0017] Moreover, as measurement], 0 degree C or less is desirable by the glass-transition-temperature [TMA (heat mechanical analysis) method of urethane (meta) acrylate system resin [A], and -20 degrees C or less are still more desirable. When 0 degree C is exceeded, cure time is large, and tackiness becomes low and is not desirable.

[0018] As with a carbon numbers of six or more used by this invention aliphatic series, or alicycle group alkyl acrylate [B] Hexyl (meta) acrylate, heptyl (meta) acrylate, octyl (meta) acrylate, Nonyl (meta) acrylate, decyl (meta) acrylate, isodecyl (meta) acrylate, Dodecyl (meta) acrylate, stearyl (meta) acrylate, Lauryl (meta) acrylate, cyclohexyl (meta) acrylate, Isobornyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, tricyclo deca nil (meta) acrylate, etc. are mentioned, and isodecyl (meta) acrylate, lauryl (meta) acrylate, and cyclohexyl (meta) acrylate are used suitably especially.

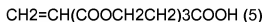
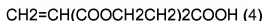
[0019] about the loadings of the above-mentioned urethane (meta) acrylate system resin [A], aliphatic series, or alicycle group alkyl acrylate [B], it is desirable that [A]: [B] is 10:90-95:5 -- further -- it is desirable that it is 50:50-80:20. If adhesion worsens under in the above-mentioned range in the loadings of [A] and the loadings of [A] cross the above-mentioned range on the other hand, coating nature will worsen and a problem will arise practically.

[0020] It is also possible to use an ethylenic unsaturated monomer for the purpose of further

adhesive improvement etc. in this invention in addition to the above [B]. Also in it, monofunctional (meta) acrylate is effective and Methyl (meta) acrylate, Ethyl (meta) acrylate, phenoxy ethyl (meta) acrylate, Glycerol mono-(meta) acrylate, glycidyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, n-butyl (meta) acrylate, Benzyl (meta) acrylate, phenol ethyleneoxide denaturation (n= 2) (meta) acrylate, Nonyl phenol propylene oxide denaturation (n= 2.5) (meta) acrylate, 2-(meta) acryloyloxy ethyl acid phosphate, furfuryl (meta) acrylate, Carbitol (meta) acrylate, benzyl (meta) acrylate, Butoxy ethyl (meta) acrylate, allyl compound (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, 2-phenoxy 2-hydroxypropyl (meta) acrylate, 2-hydroxy 3-phenoxy propyl (meta) acrylate, 3-chloro 2-hydroxypropyl (meta) acrylate, etc. are mentioned.

[0021] In addition, the Michael addition product of acrylic acid or 2-acryloyloxyethyl dicarboxylic acid monoester is also mentioned. As a Michael addition product of acrylic acid, an acrylic acid dimer [following the (3) type], Also while a methacrylic acid dimer, an acrylic acid trimer [following the (4) type], a methacrylic acid trimer, an acrylic acid tetramer [following the (5) type], a methacrylic acid tetramer, etc. are mentioned, an acrylic acid dimer is desirable.

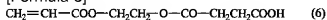
[0022]



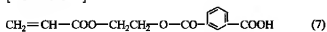
[0023] [monoester / moreover, / 2-acryloyloxyethyl dicarboxylic acid] Are a specific substituent carboxylic acid which it has, and For example, 2-acryloyloxyethyl succinic acid monoester [following the (6) type], 2-methacryloyloxy-ethyl succinic acid monoester, 2-acryloyloxyethyl phthalic acid monoester [following the (7) type], 2-methacryloyloxy-ethyl phthalic acid monoester, 2-acryloyloxyethylhexahydrophthalic acid monoester [following the (8) type], 2-methacryloyloxy ethylhexahydrophthalic acid monoester etc. is mentioned and it is 2-acryloyloxyethylhexahydrophthalic acid monoester preferably. Furthermore, in addition to this, oligoester acrylate [following the (9) type] can be mentioned.

[0024]

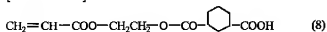
[Formula 3]



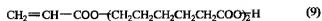
[Formula 4]



[Formula 5]



[Formula 6]



[0025] Moreover, in this invention, 2 organic-functions (meta) acrylate and the acrylate (meta) of three or more organic functions can also be used together in addition to said monofunctional (meta) acrylate. As 2 organic-functions (meta) acrylate, for example Ethylene glycol di(metha) acrylate, Diethylene GURIKORUJI (meta) acrylate, tetraethylene glycol di(metha)acrylate, Pori ethylene glycol di(metha)acrylate, propyleneglycol di(meth) acrylate, Dipropylene GURIKORUJI (meta) acrylate, Pori propyleneglycol di(meth) acrylate, Butylene glycol di (metha)acrylate, neopentyl glycol di(metha)acrylate, Ethyleneoxide denaturation bisphenol A type di(meth)acrylate, Propylene oxide denaturation bisphenol A type di(meth)acrylate, 1,6-hexanediol di(metha)acrylate, GURISERINJI (meta) acrylate, Pentaerythritol di(metha)acrylate, etyleneglycol diglycidylether di(meta)acrylate, Diethylene glycol diglycidyl ETERUJI (meta) acrylate, phthalic acid diglycidyl S TERUJI (meta) acrylate, hydroxy pivalate denaturation neopentyl glycol di(metha)acrylate, etc. are mentioned.

[0026] As acrylate (meta) of three or more organic functions For example, trimethylol propane bird (meta) acrylate, pentaerythritol bird (meta) acrylate, Pentaerythritol tetra-(meta) acrylate, dipentaerythritol penta (meta) acrylate, Dipentaerythritol hexa (meta) acrylate, bird (meta) acryloyl oxyethoxy trimethylol propane, glycerol poly glycidyl ether poly(meta) acrylate, etc. are mentioned. Also in these, the monofunctional (meta) acrylate which does not contain a hydroxyl group is desirable, and this acrylate whose molecular weight is 100 to about 300 is still more desirable.

[0027] As for especially the loadings when using this ethylenic unsaturated monomer together, 5 to 30 weight % is desirable two to 50weight % to aliphatic series or alicycle group alkyl acrylate [B]. At less than 2 weight %, these loadings are deficient in a combined effect, and if they exceed 50 weight %, they cause an adhesive fall or aggravation of compatibility and are not desirable.

[0028] In this invention, it is desirable to use a photopolymerization initiator together further, and as this photopolymerization initiator Especially if a radical is generated according to an operation of light, will not be limited, but specifically 4-phenoxy dichloro acetophenone, 4-t-butyl dichloro acetophenone, Diethoxy acetophenone, 2-hydroxy 2-methyl 1-phenylpropane 1-ON, 1-(4-iso propylene phenyl)-2-hydroxy isobutane 1-ON, 1-(4-dodecyl phenyl)-2-hydroxy isobutane 1-ON, 4 -(2-hydroxy ethoxy)- Phenyl (2-hydroxy 2-propyl) ketone, 1-hydroxy cyclohexyl phenyl ketone, 2-methyl 1-[4-(methyl thio) phenyl]-2-morpholino propane 1, benzoin, Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, Benzoin isobutyl ether, benzyl dimethyl ketal, benzophenone, benzoylbenzoic acid, benzoylbenzoic acid methyl, 4-phenyl benzophenone, hydroxy benzophenone, 4-benzoyl 4'-methyl diphenyl sulfide, 3 and 3'-dimethyl 4-methoxybenzophenone, thioxanthone, 2-KURORU thioxanthone, 2-methylthioxanthone, 2, 4-dimethylthioxanthone, Isopropylthioxanthone, camphor quinone,

dibenzosulfone, 2-ethylantraquinone, 4', 4"-diethyl isophthalophenone, 3, 3', 4, and 4'-tetra-(t-butyl par oxycarbonyl) benzophenone, alpha-ASHIROKI shim ester, acyl phosphine oxide, methylphenylglyoxylate, Benzyl, 9, 10-phenanthrene quinone, 4-(2-hydroxy ethoxy) phenyl (2-hydroxy 2-propyl) ketone, etc. are mentioned. Especially Benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone, Benzoyl isopropyl ether, 4 -(2-hydroxy ethoxy)- Phenyl (2-hydroxy 2-propyl) ketone and 2-hydroxy 2-methyl 1-phenylpropane 1-ON is used suitably.

[0029] About the loadings of this photopolymerization initiator, it is desirable that it is 1 - 10 weight part to a total of 100 weight parts of urethane (meta) acrylate system resin [A], aliphatic series, or alicycle group alkyl (meta) acrylate [B], and it is 2 - 5 weight part more preferably. Hardenability improves and is useless, even if these loadings become very slow in under 1 weight part in the cure rate in the case of ultraviolet curing and exceed 10 weight parts.

[0030] As an assistant of a photopolymerization initiator, furthermore, triethanolamine, tri-isopropanolamine, 4 and 4'-dimethylamino benzophenone (Michler's ketone), 4, and 4'-diethylamino benzophenone, 2-dimethylaminoethyl benzoic acid, 4-dimethylamino ethyl benzoate, It is also possible to use together 4-dimethylamino benzoic acid (n-butoxy) ethyl, 4-dimethylamino isoamyl benzoate, 4-dimethylamino benzoic acid 2-ethylhexyl, 2, 4-diethyl thioxanthone, 2, and 4-diisopropyl thioxanthone etc.

[0031] Moreover, it is also possible to blend an antioxidant, a flame retarder, an antistatic agent, a bulking agent, a leveling agent, a stabilizer, a reinforcer, a grinding agent, etc. besides the above-mentioned urethane (meta) acrylate system resin [A], aliphatic series or alicycle group alkyl (meta) acrylate [B], and a photopolymerization initiator. Furthermore, an epoxy compound, a horse mackerel lysine compound, a melamine compound, an isocyanate compound, chelate compound, etc. can be used for the compound and concrete target which have the operation which causes bridge formation with heat as a cross linking agent.

[0032] As an adhesion grant nature compound, addition of rosin, a rosin ester compound, pinene system polymer, hydrogenation petroleum resin, hydrocarbon resin, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, 3-methylpentane 1 and 3, 5-triol, etc. does not interfere, either. Can also blend a solvent suitably and as this solvent Moreover, ethyl acetate, Toluene, xylene, methanol, ethanol, butanol, acetone, It is possible for methyl isobutyl ketone, methyl ethyl ketone, cellosolves, diacetone alcohol, etc. to be mentioned, and to add about 1 to 50weight % to the total quantity of urethane (meta) acrylate system resin [A], aliphatic series, or alicycle group alkyl (meta) acrylate [B].

[0033] The pressure sensitive adhesive composition of this invention is usually applied to a base material sheet etc., practical use is presented with it as a pressure sensitive adhesive sheet, adhesive tape, etc. in many cases, it is hardened by activity energy line exposure and tackiness is made to discover it after applying to a base material.

[0034] As a base material to apply, polyvinyl chloride, polybutene, polybutadiene,

Polyurethane, an ethylene-vinylacetate copolymer, polyethylene terephthalate, Polyethylene, PORIPIRO pyrene, an ethylene-propylene copolymer, Pori methyl pentene, Bright films, such as polybutylene terephthalate, are mentioned and for the protection film use of the paint film of an automotive body especially A polyethylene film, The polyethylene film with which a weathering agent and other additives were blended The surface protection use of the rugged surface in the back grinding process of a semiconductor wafer, When expanded one in a dicing process uses for a required use The colored film in which the transparency or activity energy line penetration of polyvinyl chloride, polyethylene, polypropylene, an ethylene-propylene copolymer, an ethylene-vinylacetate copolymer, etc. which is excellent in plasticity and ductility is possible is used suitably.

[0035] Although electron rays besides electromagnetic waves, such as light, such as a far ultraviolet ray, ultraviolet radiation, a near ultraviolet ray, and an infrared radiation, X-rays, and a gamma ray, a proton line, a neutron beam, etc. can be used as this energy line, hardening by the UV irradiation from a cure rate, the ease of carrying out of acquisition of irradiation equipment, a price, etc. is advantageous. Moreover, it can also heat-treat at the temperature of about 80-200 degrees C following an activity energy line exposure. What is necessary is for about two 100 - 3000 mJ/cm just to glare as a method of carrying out UV irradiation hardening using a high-pressure mercury lamp, a metal halide lamp, a xenon lamp, a chemical lamp, etc. which emit the light of a 150-450nm wavelength band.

[0036] Since the pressure sensitive adhesive composition of this invention has removability, it can be widely used as a pressure sensitive adhesive sheet as a surface protection sheet or surface temporary sheets for immobilization, such as a metal plate, a glass plate, a plastic sheet, and a resin painted surface.

[0037]

[Example] Hereafter, a work example is given and this invention is explained still more concretely. In addition, especially, it expresses a weight basis that it is with the inside of a work example "%" and a "part", as long as there is no notice.

[0038] Urethane (meta) acrylate system resin [A] was manufactured in the following ways.
- It is isophorone diisocyanate 100.0g (0.45mol) to a urethane acrylate resin (A-1) thermometer, an agitator, a water-cooled condenser, and 4 mouth flask equipped with the nitrogen gas blowing-in mouth, A hydrogenation polybutadiene polyol 359g (0.15mol) and the hydrogenation polybutadiene polyol (the average molecular weight 1740, the iodine number 21, hydroxyl value 64.5 KOHmg/g) 266.6g (0.15mol) are taught. (The average molecular weight 2343, the iodine number 21, hydroxyl value 47.9 KOHmg/g) When it is made to react at 90 degrees C and a residual isocyanate group becomes 1.4% Lowered temperature to 70 degrees C, add 4-hydroxy butyl acrylate 43.5g (0.3mol), and it was made to react, when the residual isocyanate group became 0.3%, the reaction was ended, and urethane acrylate resin

(A-1) [glass-transition-temperature-30 degree C and average molecular weight 14,000] was obtained.

[0039] - It is isophorone diisocyanate 120.0g (0.54mol) to a urethane acrylate resin (A-2) thermometer, an agitator, a water-cooled condenser, and 4 mouth flask equipped with the nitrogen gas blowing-in mouth, When teach the hydrogenation polybutadiene polyol (the average molecular weight 2267, the iodine number 21, hydroxyl value 49.5 KOHmg/g) 833.6g (0.36mol), it is made to react at 90 degrees C and a residual isocyanate group becomes 1.6% Lowered temperature to 70 degrees C, add 2-hydroxyethyl acrylate 43.8g (0.38mol), and it was made to react, when the residual isocyanate group became 0.3%, the reaction was ended, and urethane acrylate resin (A-2) [glass-transition-temperature-25 degree C and average molecular weight 13,000] was obtained.

[0040] - It is hexamethylene di-isocyanate 112.9g (0.60mol) to a urethane acrylate resin (A-3) thermometer, an agitator, a water-cooled condenser, and 4 mouth flask equipped with the nitrogen gas blowing-in mouth, A hydrogenation polybutadiene polyol 468.6g (0.20mol) and the hydrogenation polybutadiene polyol (the average molecular weight 1740, the iodine number 21, hydroxyl value 64.5 KOHmg/g) 348.0g (0.20mol) are taught. (The average molecular weight 2343, the iodine number 21, hydroxyl value 47.9 KOHmg/g) When it is made to react at 90 degrees C and a residual isocyanate group becomes 1.8% Lower temperature to 70 degrees C, and add caprolactone denaturation acrylate ("plaque cell FA-IDDM" by a DAISERU chemistry company) 93.3g (0.405mol), and it is made to react. When the residual isocyanate group became 0.3%, the reaction was ended, and urethane acrylate resin (A-3) [glass-transition-temperature-25 degree C and average molecular weight 16,000] was obtained.

[0041] Moreover, the following was used as aliphatic series or alicycle group alkyl (meta) acrylate [B].

(B-1): octyl acrylate (B-2): -- isodecyl acrylate (B-3): -- cyclohexyl acrylate (B'-1): -- phenoxy ethyl acrylate (B'-2): -- tripropylene glycol diacrylate [0042] Work examples 1-7, a comparative example 1 - urethane (meta) acrylate system resin [A] of 3 above, aliphatic series, or alicycle group alkyl (meta) acrylate [B] It mixed with the **** loadings shown in Table 1, and four copies of photopolymerization initiators (the Ciba Specialty Chemicals make, "DAROKYUA 1173"), in addition a type ultraviolet curing adhesive mass composition were obtained further.

[0043]

[Table 1]

[A] [B] kind Content (part) Kind Content (part) Work example 1 A-1 70B-1 30 ** 2 A-2 70B-2 30 ** 3 A-3 70B-3 30 ** 4 A-1 80B-2 20 ** 5 A-2 80B-1 20 ** 6 A-3 80B-2 20 ** 7 A-1 70B-3 30 Comparative example 1 A-1 70 B'-1 30 ** 2 A-1 70 B'-2 30 ** 3 Polyisobutylene system binder 100 [0044] subsequently, it becomes an unsettled polyethylene terephthalate (PET) film

(50micro in thickness) with 25micro of thickness about the obtained constituent -- as Applied by applicator, and carry out UV irradiation, it was made to harden under the conditions of 80W [/cm] (high-pressure mercury lamp) x13cmHx1.5 m/minxPass (addition 3000mJ/cm2) with desk UV irradiation equipment (the Iwasaki Electric Co., Ltd. make, "conveyor type desk irradiation equipment"), and the adhesive sheet was obtained.

[0045] The following evaluations were carried out about this adhesive sheet. A result is shown in Table 2.

(Tackiness) The above-mentioned adhesive sheet was stuck on the SUS polish board, and two round trips and a 180-degree friction test (g/25cm) 30 minutes after were done with the 2kg roller.

[0046] (Holding power) The holding power (gap mm) 24 hours after carrying out a semi- place to JISZ0237 was measured, having applied [stuck so that the above-mentioned adhesive sheet might be stuck on a SUS polish board and area might be set to 25mm x 25mm, and] 1kg of load under the conditions of 40 degrees C and 65%RH.

[0047] (Weatherability) about the sheet used for adhesive measurement, they are the following bases about the appearance 1000 hours after a sunshine weather meter exposure -- moreover, tackiness (g/25mm) -- said -- it evaluated similarly.

O : -- **: which does not almost have change of a color tone -- x: which is a little tinged with the yellow taste -- it has discolored remarkably [0048]

[Table 2]

	tackiness	Holding power	weatherability (g/25mm)	(gap mm)	appearance	Tackiness (g/25mm)
Work example 1	1250	0.00	1200	** 2	1300	0.00
1250	0.00	1200	** 3	1500	0.05	1400
** 4	1350	0.00	1300	** 5	1500	0.00
1450	** 6	1500	0.05	1300	** 7	1400
0.05	1350	Comparative	Example 1	Since it Became Cloudy and Phase Separation Happened	It does not measure but	is
** 2.	400	0.5	** 100	** 3	900	0.05
x 30	>	[0049]				

[Effect of the Invention] [the activity energy hardening type pressure sensitive adhesive composition of this invention] [the end isocyanate group content compound of the reactant of a hydrogenation polybutadiene polyol (a1) and a polyisocyanate (a2)] The urethane (meta) acrylate system resin [A] of specified structure obtained by making hydroxyl group content (meta) acrylate (a3) react, with a carbon numbers of six or more aliphatic series, or alicycle group alkyl (meta) acrylate [B] is included, and sake, it excels in adhesive strength with a base material, and weatherproof balance. It is useful as an object for the protection films of the goods which consist of various base materials, such as a protection film use for automotive bodies, and a polyester film, a metal, glass.

[Translation done.]